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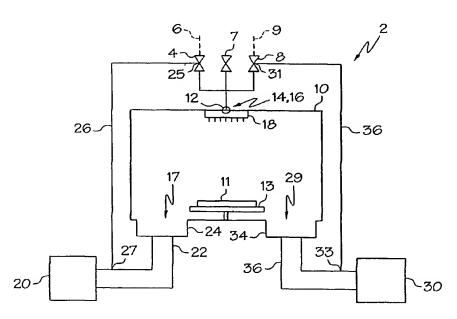
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(54) Title: ATOMIC LAYER DEPOSITION APPARATUS AND PROCESS



(57) Abstract: An apparatus (2) and process for atomic layer deposition that minimizes mixing of the chemicals and reactive gases is disclosed. The first precursor and second precursor are only mixed with other chemicals and reactive gases when and where desired by installing and monitoring a dispensing fore-line (26). Also, independent and dedicated chamber outlets (17, 29), isolation valves (24, 34), exhaust fore-lines (22, 36), and exhaust pumps (20, 30) are provided that are activated for the specific gas when needed.



03/033762 A1

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-1-

ATOMIC LAYER DEPOSITION APPARATUS AND PROCESS

The present invention relates to atomic layer deposition. More specifically, the present invention relates to an apparatus and process for improving the performance of an atomic layer deposition chamber.

A method of depositing very thin films is atomic layer deposition (ALD). This method has several advantages over tradition chemical vapor deposition. It can be performed at lower temperatures, uses a wide range of precursors, produces very thin films, inherently obtains 100% step coverage, and can be used to "microengineer" complex film matrices.

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In ALD, individual precursors are pulsed onto the surface of a wafer in a sequential manner, without mixing the precursors in the gas phase. Each individual precursor reacts with the surface to form an atomic layer in a way that only one layer can form at a time. The surface reaction occurs such that the reaction is complete, and permits no more than one layer at a time to be deposited. This occurs no matter how many molecules are applied to the surface in an overdosing mode. The films are built up by introducing short bursts of gases in rapid cycles.

According to recognitions of the present inventors, two problems occur with the ALD method. One problem concerns the diversion of the flow of liquid precursors introduced in a vapor phase. During ALD processing using a liquid delivery system, it is necessary to keep an established flow of the liquid precursor in a vapor phase. In order to keep the flow active, the flow must be diverted to a fore-line of the ALD chamber when the liquid precursor is not needed in the deposition process. When the opposing gas is pulsed, the unreacted chemical is mixed in the fore-line with the diverted chemical and reacts causing a build up in the fore-line. The build up can be severe and clogs the fore-line. A second problem concerns the reaction of the gases. Process gases are introduced individually for the ALD process and disposed of through the same fore lines causing the gases or vapors to react with one another.

Accordingly, there is a need for an ALD apparatus and process that minimizes clogging of the fore-line of the diverted liquid precursor. There is also a need in the art to

-2-

control any area that is common to the reactive gases or vapors in a way to minimize any unwanted reaction.

These needs are met by the present invention wherein an improved ALD apparatus and process are provided. The present invention fulfills the first need of minimizing clogging of the fore-line by providing an ALD apparatus and process that allows separate chemicals to only mix when and where desired by installing and monitoring a second fore-line. The present invention fulfills the second need of minimizing the reaction of the gases in the pump lines, by allowing the reactive gases or vapors to be removed from the process reactor chamber without coming in contact with one another in an area that would create an unwanted reaction of the process gases or vapors. This is accomplished by providing independent and dedicated pumping lines and corresponding isolation valves that are activated for the specific gas when needed. The separate pump lines allow the gas to be exhausted in a manner that minimizes possible unwanted reaction of the reactive gases. Accordingly, it is an object of the present invention to provide an improved ALD apparatus and process using dispensing fore-lines and a second exhaust path in order to prevent clogging of the exhaust fore-line.

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The following detailed description of the preferred embodiments of the present invention can be best understood when read in conjunction with the following drawings, where like structure is indicated with like reference numerals and in which:

Figure 1 presents an illustration of an ALD apparatus according to one embodiment of the present invention;

Figure 2 presents an illustration of an ALD apparatus according to another embodiment of the present invention;

Figure 3 presents an illustration of an ALD apparatus according to still another embodiment of the present invention;

Figure 4 presents an illustration of an ALD apparatus according to yet another embodiment of the present invention; and

Figure 5 presents an illustration of an ALD apparatus according to yet another embodiment of the present invention.

Referring initially to Fig. 1, an ALD apparatus 2 according to one embodiment of the present invention is illustrated. Fig. 1 illustrates an ALD apparatus 2 comprising a

-3-

process reactor chamber 10, a first dispensing valve 4, a second dispensing value 8, an isolation valve 24, an exhaust fore-line 22, an exhaust pump 20, and a dispensing fore-line 26. The process reactor chamber 10 includes a first precursor inlet 14, a second precursor inlet 16, and a first chamber outlet 17. The first dispensing valve 4 is coupled to the first precursor inlet 14 of the process reactor chamber 10. The second dispensing valve 8 is coupled to the second precursor inlet 16 of said process reactor chamber 10. The isolation valve 24 is directly coupled to the first chamber outlet 17 of the process reactor chamber 10. The exhaust pump 20 is coupled to the isolation valve 24 by the exhaust fore-line 22, defining an exhaust path. The dispensing fore-line 26 comprises a first end 25 and a second end 27. The first end 25 is coupled to the first dispensing valve 4 and the second end 27 is coupled to the exhaust pump 20.

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The first dispensing valve 4 allows a first precursor 6 to flow into the process reactor chamber 10 through a first precursor inlet 14. A continuous flow of the first precursor 6 must be maintained. Therefore, the first dispensing valve 4 selectively diverts the direction of the first precursor 6 to the first precursor inlet 14 of the process reactor chamber 10. When the first precursor 6 is not diverted into the process reactor chamber 10, it is sent to the exhaust pump 20 via a dispensing fore-line 26. The dispensing fore-line 26 is used to discard the first precursor 6 when it is not diverted into the first precursor inlet 14. The dispensing fore-line 26 may be used to isolate the first precursor 6 from other chemicals, precursors, and exhausts that would otherwise mix with the first precursor 6 and potentially cause clogging of the first exhaust fore-line 22. Thus, the exhaust fore-line 22 remains clean and flow remains stable and consistent.

The process reactor chamber 10 comprises a first precursor inlet 14, a second precursor inlet 16, a heater 13, a wafer 11, and a shower head device 18. The first precursor inlet 14 and second precursor inlet 16 can share a common opening 12 or alternatively have separate openings. The first precursor inlet 14 may direct the first precursor 6 through a shower head device 18 that distributes the first precursor 6 into the process reactor chamber 10. Once in the process reactor chamber 10 the first precursor 6 is absorbed onto the surface of a wafer 11. The wafer rests on a heater 13. The manner in which absorption of the precursor is achieved is beyond the scope of the present invention

-4-

and is well known in the art. It may be gleaned from any one of a number of teachings relating to atomic layer deposition.

After the first precursor 6 is absorbed onto the wafer 11, unreacted first precursor is purged out of the process reactor chamber 10 by introducing a purge gas via the purge valve 7 into the chamber outlet 17. Unreacted first precursor flows directly into the isolation valve 24 where unreacted first precursor is transferred to the exhaust pump 20 via the exhaust fore-line 22.

The first precursor 6 and second precursor 9 are introduced in separate intervals. Once unreacted first precursor is purged from the process reactor chamber 10 through use of the purging valve 7, the second dispensing valve 8 allows for the introduction of the second precursor 9 into the second precursor inlet 16 and ultimately into the process reactor chamber 10. The second precursor inlet 16 directs the second precursor 9 through a shower head device 18 that distributes the second precursor 9 into the process reactor chamber 10. The second precursor 9 then reacts with the layer formed on the wafer 11 from the first precursor 6, creating a monolayer of film on the wafer 11.

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Unreacted second precursor is purged from the process reactor chamber 10, using the purging valve 7, into the chamber outlet 17. Unreacted second precursor flows directly into the isolation valve 24 where unreacted second precursor is transferred to the exhaust pump 20 via the exhaust fore-line 22.

This process of the introduction, reaction, and purging alternating the first precursor 6 with the second precursor 9 is performed at a high rate of speed with continuous successions.

For the purposes of describing and defining the present invention, it is noted that the precise mechanism by which the molecules of the first precursor adhere to the surface of the semiconductor substrate is not the subject of the present invention. The mechanism is merely described herein as 'absorption.' The generic term 'absorption' is intended to cover absorption, adsorption, and any other similar mechanisms by which the precursor may form a monolayer upon the surface of the wafer 11.

The embodiment of the present invention illustrated in Fig. 2 differs from Fig.1 in that it utilizes a dispensing pump 28. In this embodiment, the first end 25 of the dispensing fore-line 26 is coupled to the dispensing valve 4. The second end 27 of the

-5-

dispensing fore-line 26 is coupled to the dispensing pump 28. The dispensing pump 28 collects the undiverted first precursor 6 so that the undiverted first precursor 6 is isolated from other chemicals, precursors, and exhausts that would otherwise mix with the first precursor 6 and potentially cause clogging of the first exhaust fore-line 22. Thus, the exhaust fore-line 22 remains clean and flow remains stable and consistent.

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The embodiment of Fig. 3 differs from that illustrated in Fig. 2 because the second isolation valve 34, the second exhaust fore-line 36, and the second exhaust pump 30 are shown, thus defining a second exhaust path. This second exhaust path is constructed to keep the unreacted first precursor and the unreacted second precursor separate. Thereby, reducing the possibility of mixing and clogging the either of the exhaust fore-lines 22, 36. The second isolation valve 34, the second exhaust fore-line 36, and the second exhaust pump 30 operate in a similar manner as the first isolation valve 24, the first exhaust fore-line 22, and the first exhaust pump 20. After the second precursor 9 is absorbed onto the wafer 11, the unreacted second precursor is purged out of the process reactor chamber 10 by introducing a purge gas via the purge valve 7 into the second chamber outlet 29. The unreacted second precursor flows directly into the second isolation valve 34 where the unreacted second precursor is transferred to the second exhaust pump 30 via the second exhaust fore-line 36.

The embodiment in Fig. 3 also differs from that illustrated in Fig. 2 because the dispensing fore-line 26 is connected to the first exhaust path. Specifically, the dispensing fore-line 26 is connected to the first exhaust pump 20. The dispensing valve could alternatively be coupled to the first exhaust fore-line 22 or directly to a dispensing pump 28 as illustrated in Fig. 2.

The embodiment of Fig. 4 differs from that of Fig. 3 because a second dispensing fore-line 36 is extended from the second dispensing valve 8 to the second exhaust path, specifically the second exhaust fore-line 33. The second dispensing fore-line 36 can alternatively be directly connected to the second exhaust pump 30, similar to the embodiment of Fig. 1 or connected to a second dispensing pump, similar to the embodiment of Fig. 2. The second dispensing pump would operate in a similar manner as the first dispensing pump 28 described above. The second dispensing pump collects the undiverted second precursor 9 so that the undiverted second precursor 9 is isolated from

-6-

other chemicals, precursors, and exhausts that would otherwise mix with the second precursor 9 and potentially cause clogging of the second exhaust fore-line 36. Thus, the second exhaust fore-line 36 remains clean and flow remains stable and consistent.

The second dispensing fore-line 36 operates in a similar manner as the first dispensing fore-line 26. The second dispensing fore-line 36 is used to discard the second precursor 9 when it is not diverted into the second precursor inlet 16. The second dispensing fore-line 36 may be used to isolate the second precursor 9 from other chemicals, precursors, and exhausts that would otherwise mix with the second precursor 9 and potentially cause clogging of the second exhaust fore-line 33. Thus, the second exhaust fore-line 33 remains clean and flow remains stable and consistent.

Fig. 5 differs from the previous figures because it does not show the first dispensing fore-line 26 or the second dispensing fore-line 36. Therefore, only the two separate exhaust paths are depicted.

Having described the invention in detail and by reference to preferred embodiments thereof, it will be apparent that modifications and variations are possible without departing from the scope of the invention defined in the appended claims. More specifically, although some aspects of the present invention are identified herein as preferred or particularly advantageous, it is contemplated that the present invention is not necessarily limited to these preferred aspects of the invention.

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-7-

CLAIMS

5 1. An atomic layer deposition apparatus comprising:

a process reactor chamber comprising a first precursor inlet, a second precursor inlet, and a first chamber outlet;

a first dispensing valve coupled to said first precursor inlet of said process reactor chamber;

a second dispensing valve coupled to said second precursor inlet of said process reactor chamber;

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a first exhaust path coupled to said process reactor chamber configured to be selectively isolated from said process reactor chamber; and

a first dispensing fore-line comprising a first end and a second end, wherein said first end is coupled to said first dispensing valve and said second end of said first dispensing fore-line is coupled to one of said first exhaust path or a first dispensing pump.

- 2. An apparatus as claimed in claim 1, wherein said second end of said first dispensing fore-line is coupled to said first exhaust path.
 - 3. An apparatus as claimed in claim 1, wherein said first exhaust path further comprises a first exhaust pump, a first isolation valve, and a first exhaust fore-line, wherein said first exhaust pump is coupled to said first isolation valve by said first exhaust fore-line.

PCT/US02/32741

-8-

- 4. An apparatus as claimed in claim 3, wherein said first exhaust path is isolated from said process reactor chamber when said first isolation valve is in a closed state.
- 5. An apparatus as claimed in claim 3, wherein said first isolation valve is directly coupled to a first chamber outlet of said process reactor chamber.
 - 6. An apparatus as claimed in claim 3, wherein said second end of said first dispensing fore-line is coupled to said first isolation valve of said first exhaust path.
- 7. An apparatus as claimed in claim 3, wherein said second end of said first dispensing fore-line is coupled to said first exhaust pump of said first exhaust path.
 - 8. An apparatus as claimed in claim 3, wherein said second end of said first dispensing fore-line is coupled to said first exhaust fore-line of said first exhaust path.

- 9. An apparatus as claimed in claim 1, wherein said apparatus further comprises a second exhaust path coupled to a second chamber outlet.
- 10. An apparatus as claimed in claim 9, wherein said second exhaust path comprises a second exhaust pump, a second isolation valve, and a second exhaust fore-line, wherein said second exhaust pump is coupled to said second isolation valve by said second exhaust fore-line.
- 11. An apparatus as claimed in claim 9, wherein said second exhaust path is isolated from said process reactor chamber when said isolation valve is in a closed state.
 - 12. An apparatus as claimed in claim 9, wherein said second isolation valve is directly coupled to a second chamber outlet of said process reactor chamber.
- 30 13. An apparatus as claimed in claim 1, wherein said second end of said first dispensing fore-line is coupled to said first dispensing pump.

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An apparatus as claimed in claim 1, wherein said apparatus further comprises a second dispensing fore-line comprising a first end and a second end, wherein said first end

PCT/US02/32741

is coupled to said second dispensing valve and said second end of said second dispensing

-9-

- 5 fore-line is coupled to a second exhaust path.
 - An apparatus as claimed in claim 14, wherein said second exhaust path comprises 15. a second exhaust pump, a second isolation valve, and a second exhaust fore-line, wherein said second exhaust pump is coupled to said second isolation valve by said second exhaust fore-line.
 - 16. An apparatus as claimed in claim 15, wherein said second end of said second dispensing fore-line is coupled to said second isolation valve of said second exhaust path.
- 17. An apparatus as claimed in claim 15, wherein said second end of said second 15 dispensing fore-line is coupled to said second exhaust pump of said second exhaust path.
 - 18. An apparatus as claimed in claim 15, wherein said second end of said second dispensing fore-line is coupled to said second exhaust fore-line of said second exhaust path.
 - An apparatus as claimed in claim 1, wherein said apparatus further comprises a 19. second dispensing fore-line comprising a first end and a second end, wherein said first end is coupled to said second dispensing valve and said second end of said second dispensing fore-line is coupled to a second dispensing pump.
 - An apparatus as claimed in claim 1, wherein said process reactor chamber 20. comprises a second chamber outlet.
- 21. An apparatus as claimed in claim 1, wherein said apparatus further comprises a 30 first vapor supply coupled to said first precursor inlet.

-10-

PCT/US02/32741

- 22. An apparatus as claimed in claim 1, wherein said apparatus further comprises a second vapor supply coupled to said second precursor inlet.
- 5 23. An apparatus as claimed in claim 1, wherein said first precursor inlet and said second precursor inlet share a common opening.
 - 24. An apparatus as claimed in claim 1, wherein said first precursor inlet and said second precursor inlet have separate openings.
 - 25. An apparatus as claimed in claim 1, wherein said apparatus comprises a purging valve.
- 26. An apparatus as claimed in claim 1, wherein said process reactor chamber further includes a shower head device.
 - 27. An atomic layer deposition apparatus comprising:

a process reactor chamber;

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- a first isolation valve directly coupled to a first chamber outlet of said process reactor;
- a first exhaust pump coupled to said first isolation valve by a first exhaust fore-line;
 - a second isolation valve directly coupled to a first chamber outlet of said process reactor; and
- a second exhaust pump coupled to said second isolation valve by a second exhaust fore-line.

-11-

- 28. An apparatus as claimed in claim 27, wherein said apparatus comprises a purging valve.
- 5 29. An apparatus as claimed in claim 27, wherein said process reactor chamber further includes a shower head device.
 - 30. An apparatus as claimed in claim 27, wherein said process reactor chamber comprises a first precursor inlet, a second precursor inlet, a first chamber outlet, and a second chamber outlet.
 - 31. An apparatus as claimed in claim 30, wherein said apparatus further comprises a first vapor supply coupled to said first precursor inlet.
- 32. An apparatus as claimed in claim 30, wherein said apparatus further comprises a second vapor supply coupled to said second precursor inlet.
 - 33. An apparatus as claimed in claim 30, wherein said first precursor inlet and said second precursor inlet share a common opening.
- 20 34. An apparatus as claimed in claim 30, wherein said first precursor inlet and said second precursor inlet have separate openings.
 - 35. A process for atomic layer deposition comprising:

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25 introducing a first precursor into a first precursor inlet of a process reactor chamber;

controlling said process reactor chamber for absorption of said first precursor onto a substrate;

purging said chamber of unabsorbed first precursor;

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-12-

introducing a second precursor into a second precursor inlet of said process reactor chamber;

PCT/US02/32741

5 controlling said process reactor chamber for reaction of said second precursor with said first precursor; and

purging said process reactor chamber of unreacted second precursor.

- 36. A process as claimed in claim 35, wherein said process further comprises controlling a first dispensing valve to alternate between a first inlet state and a first bypass state, wherein said first inlet state is characterized by diversion of said first precursor to said first precursor inlet of said process reactor chamber and wherein said first bypass state is characterized by diversion of said first precursor to a first fore-line coupled to said first dispensing valve.
 - 37. A process as claimed in claim 36, wherein said controlling of said first dispensing valve further comprises maintaining a continuous flow of said first precursor.
- 20 38. A process as claimed in claim 36, wherein said process further includes the step of emptying said first precursor diverted to said first fore-line to a first exhaust pump coupled to said fore-line.
- 39. A process as claimed in claim 36, wherein said process further includes the step of
 emptying said first precursor diverted to said fore-line to said first exhaust path coupled to
 said first fore-line.
 - 40. A process as claimed in claim 36, wherein said process further includes the step of emptying said first precursor diverted to said first fore-line to a first dispensing pump coupled to said first fore-line.

-13-

- 41. A process as claimed in claim 35, wherein said process further comprises controlling a second dispensing valve to alternate between a second inlet state and a second bypass state, wherein said second inlet state is characterized by diversion of a second precursor to a second precursor inlet of a process reactor chamber and wherein said second bypass state is characterized by diversion of said second precursor to a second fore-line coupled to said second dispensing valve.
- 42. A process as claimed in claim 41, wherein said controlling of said first dispensing valve further comprises maintaining a continuous flow of said second precursor.
- 43. A process as claimed in claim 41, wherein said process further includes the step of emptying said second precursor diverted to said second fore-line to a second exhaust pump coupled to said second fore-line.
- 15 44. A process as claimed in claim 41, wherein said process further includes the step of emptying said second precursor diverted to said second fore-line to said second exhaust path coupled to said second fore-line.
- 45. A process as claimed in claim 41, wherein said process further includes the step of emptying said second precursor diverted to said second fore-line to a second dispensing pump coupled to said second fore-line.
 - 46. A process as claimed in claim 35, wherein said process further includes diverting selectively said first precursor into said first precursor inlet of said process reactor chamber while maintaining a continuous flow of said first precursor.
 - 47. A process as claimed in claim 35, wherein said process further includes diverting selectively said second precursor into said second precursor inlet of said process reactor chamber while maintaining a continuous flow of said second precursor.

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-14-

- 48. A process as claimed in claim 35, wherein said purging said process reactor chamber of said unabsorbed first precursor further comprises opening a first isolation valve coupled to a first exhaust outlet in said reactor chamber.
- 5 49. A process as claimed in claim 48, wherein said first isolation valve and said first exhaust outlet define said first exhaust path.
- 50. A process as claimed in claim 35, wherein said purging said process reactor chamber of said unreacted second precursor further comprises opening a second isolation
 valve coupled to a second exhaust outlet in said reactor chamber.
 - 51. A process as claimed in claim 50, wherein said second isolation valve and said second exhaust outlet define a second exhaust path.
- 15 52. A process as claimed in claim 35, wherein said purging said process reactor chamber of said unabsorbed first precursor further comprises opening a first isolation valve coupled to a first exhaust outlet in said reactor chamber and said purging said process reactor chamber of said unreacted second precursor further comprises opening a second isolation valve coupled to a second exhaust outlet in said reactor chamber.

53. A process as claimed in claim 52, wherein said first isolation valve is opened while said second isolation valve is closed.

- 54. A process as claimed in claim 52, wherein said second isolation valve is opened while said first isolation valve is closed.
 - 55. A process as claimed in claim 52, wherein said first isolation valve is opened while said second isolation valve is closed and said second isolation valve is opened while said first isolation valve is closed.

-15-

- 56. A process as claimed in claim 52, wherein said first isolation valve is independent of said second isolation valve.
- 57. A process as claimed in claim 52, wherein said first exhaust outlet is independent of said second exhaust outlet.
 - 58. A process as claimed in claim 35, wherein said purging said process reactor chamber by opening a first exhaust path to remove unabsorbed first precursor from said process reactor chamber.

59. A process as claimed in claim 35, wherein said purging said process reactor chamber by opening a second exhaust path to remove unreacted second precursor from said process reactor chamber.

15 60. A process as claimed in claim 35, wherein said purging said process reactor chamber by opening a first exhaust path to remove unabsorbed first precursor from said process reactor chamber and said purging said process reactor chamber by opening a second exhaust path to remove unreacted second precursor from said process reactor chamber.

61. A process as claimed in claim 60, wherein said first exhaust path is opened while said second exhaust path is closed.

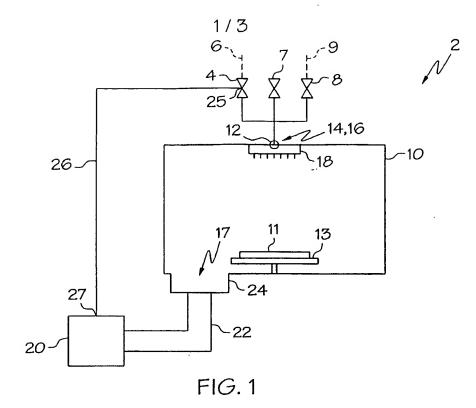
- 62. A process as claimed in claim 60, wherein said second exhaust path is opened while said first exhaust path is closed.
 - 63. A process as claimed in claim 60, wherein said first exhaust path is opened while said second exhaust path is closed and said second exhaust path is opened while said first exhaust path is closed.

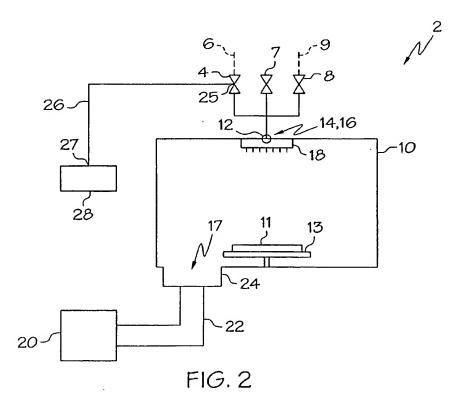
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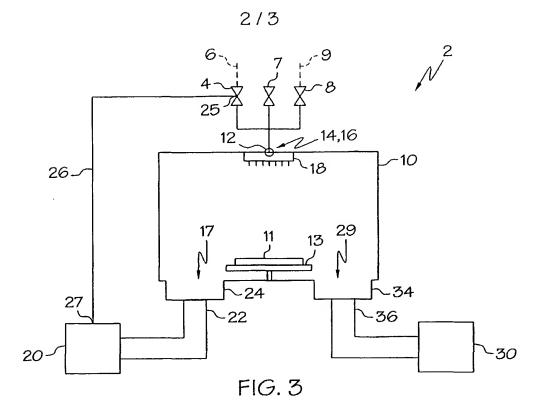
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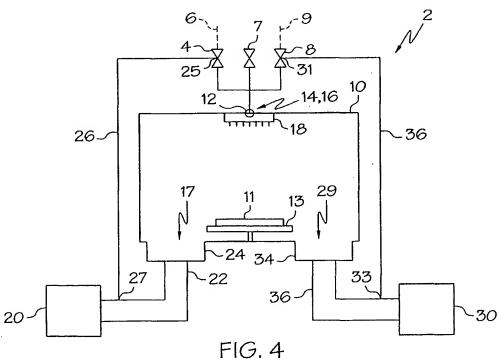
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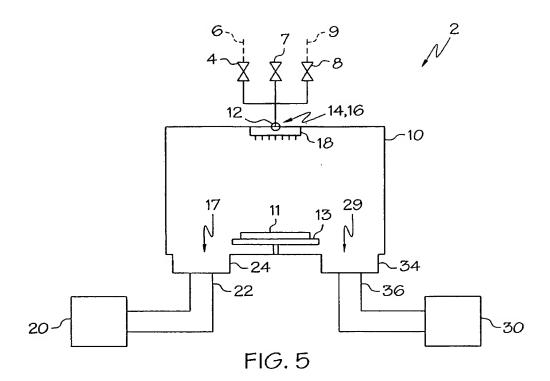
64. A process as claimed in claim 60, wherein said first exhaust path is independent of said second exhaust path.











INTERNATIONAL SEARCH REPORT

International Application No PCT/US 02/32741

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C23C16/44 C23C16/455

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

 $\begin{array}{ccc} \text{Minimum documentation searched (classification system followed by classification symbols)} \\ IPC 7 & C23C & C30B \end{array}$

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, WPI Data, EPO-Internal, IBM-TDB

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 674 563 A (SOUTOME YOSHIHIRO ET AL) 7 October 1997 (1997-10-07)	1-5,7, 21,22,24
Y	column 10, line 35 -column 11, line 57; figure 1	6,8,20, 25,26,34
X	EP 0 651 432 A (KYOHARA MASAKO) 3 May 1995 (1995-05-03)	1,13,23
Y	page 4, line 45 -page 5, line 12; figure 1	20,25,26
X	PATENT ABSTRACTS OF JAPAN vol. 013, no. 481 (E-838), 31 October 1989 (1989-10-31) & JP 01 189114 A (NEC CORP), 28 July 1989 (1989-07-28)	27,30-33
Y	abstract -/	28,29,34

X Further documents are listed in the continuation of box C.	Patent family members are listed in annex.			
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Date of the actual completion of the international search	Date of mailing of the international search report			
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International Application No PCT/US 02/32741

In indication, where appropriate, of the relevant passages 72 B1 (LEE SANG-IN ET AL) 70 B1 (2001-08-07) 71 Ine 50 -column 6, line 29; 72 B1 (LEE SANG-IN ET AL) 73 B1 (LEE SANG-IN ET AL) 74 B1 (2001-08-07) 75 B1 COLUMN 6, line 29; 76 B1 B1 COLUMN 6, line 29; 77 B1 B1 COLUMN 6, line 29; 78 B1 COLUMN 6, line 20; 78 B1 COLUMN 7, line 22; 78 B1 COLUMN 7, line 22;	9,11,12, 26,28, 29,36-64 9,11,12, 20,48-64
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